

Massive Volcanism in the Altiplano-Puna Volcanic Plateau and Formation of the Huge Atacama Desert Nitrate Deposits: A Case for Thermal and Electric Fixation of Atmospheric Nitrogen

JORGE OYARZUN

Departamento de Minas, Facultad de Ingeniería and CEAZA, Universidad de La Serena, Casilla 554, La Serena, Chile

AND ROBERTO OYARZUN¹

Departamento de Cristalografía y Mineralogía, Facultad de Ciencias Geológicas, Universidad Complutense, 28040 Madrid, Spain

Abstract

The origin of the giant nitrate deposits of the Atacama Desert (Chile) is a controversial issue. At a global scale, the Atacama Desert nitrates constitute a rare singularity because no equivalent deposits are found anywhere else. Previous hypotheses for origin of the Chilean nitrates have failed to recognize the importance of the 70,000 km² Late Miocene to present Altiplano-Puna volcanic plateau (APVP), only 50–200 km eastward from the nitrate deposits. We argue that the extrusion of a volume of over 10⁴ km³ of pyroclastic rocks at the APVP may have created the conditions to induce thermal and electric fixation of an estimate of 2800 Mt of atmospheric nitrogen in the form of NO₃. This figure exceeds the amount of nitrogen required to account for the Atacama Desert nitrate deposits. Thus, the origin of the nitrate deposits may be found in an unusual combination of hyper-arid conditions (vital for the final stabilization and preservation of the NaNO₃ mineral phase) and massive volcanism (key to fixation of large amounts of atmospheric nitrogen). Volcanic eruptions have far more environmental implications than usually assumed, decisively contributing to the global cycles of many chemical elements and compounds. For example, nitrogen fixation by volcanic activity could also explain the current excess of NO_x compounds in the pristine marine atmosphere of the mid-Pacific, a realm conspicuously surrounded by the world's largest concentration of active volcanoes.

Introduction

THE ORIGIN OF THE extensive natural nitrate (NaNO₃) deposits of Chile's Atacama Desert poses one of the most intriguing, unresolved problems in the Earth sciences. The nitrate deposits (e.g., Erickson, 1981, 1983, 1993) are emplaced along a narrow, N-S, ~700 km long belt at an altitude of ~1000 m, hosting some 250 Mt of nitrates (Fig. 1). Despite the abundance of the components (Na, N, O), only minor occurrences of natural nitrate have been reported elsewhere. Thus, the Chilean nitrates constitute a world-class geological singularity lacking, despite several attempts, a definitive explanation.

From a geological and physiographic point of view, the region can be divided into five main N-S-trending structural blocks (Fig. 2): (1) the Coastal Ranges, formed by Mesozoic andesitic volcanic

rocks and granitoids; (2) the Western Depression, where the nitrate districts are present; (3) the Domeyko Mountains, with Mesozoic to Cenozoic sedimentary, volcanic, and intrusive rocks; (4) the pre-Andean depressions, including the large Atacama Salar; and (5) the giant Altiplano-Puna volcanic plateau (APVP). The APVP outcrop area in the Andean segment of the study area (Fig. 1) is about 70,000 km², with over 10⁴ km³ of erupted volume, which makes the plateau the largest young ignimbrite province on Earth (e.g., Allmendinger et al., 1997; Babeyko et al., 2002). Ignimbrite activity in the APVP started at about 10 Ma and continued strongly until ~1 Ma (Babeyko et al., 2002; Schmitt et al., 2002). Single ignimbrite eruptions of silicic andesitic to dacitic composition (63–68% SiO₂) exceeded 1000 km³ in volume, erupted from caldera systems, and constitute the dominant late Miocene–Pliocene volcanic deposits on the plateau (De Silva,

¹Corresponding author; email: oyarzun@geo.ucm.es

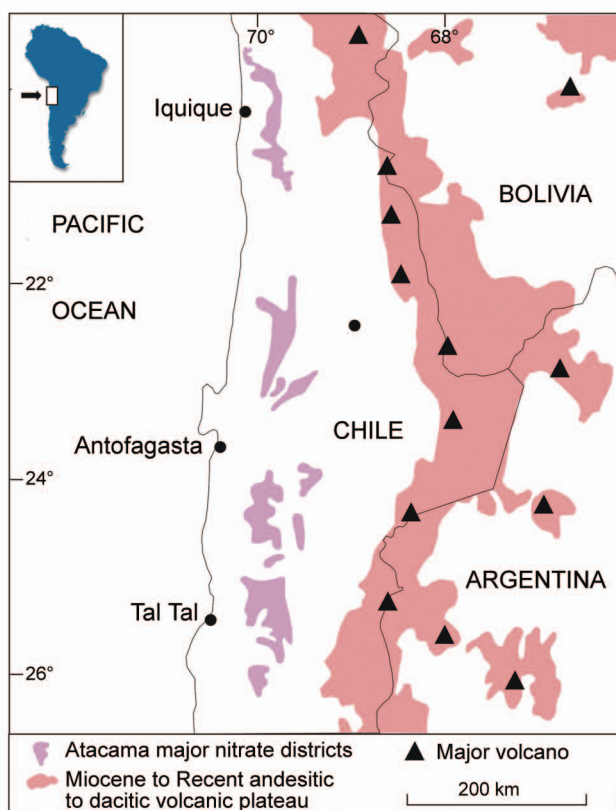


FIG. 1. Location of nitrate deposits and the Altiplano-Puna volcanic plateau (after Ericksen, 1993; Allmendinger et al., 1997).

1989; Allmendinger et al., 1997; Schmitt et al., 2002).

On the other hand, the Atacama nitrate deposits (Fig. 1) began to form in Miocene time (Ericksen, 1993), and are mined from the so-called caliche beds, a deposit that contains high nitrate and iodine concentrations (6–9% and 0.03–0.06%, respectively). Typical caliche beds are mainly made up of halite and nitratine (NaNO_3), with minor darpskite ($\text{Na}_3(\text{SO}_4)(\text{NO}_3) \cdot \text{H}_2\text{O}$), humberstonite ($\text{K}_3\text{Na}_7\text{Mg}_2(\text{SO}_4)_6(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), anhydrite, glauberite, and bloedite, together with subordinate iodates, borates, chromates, zeolites, and calcite (Ericksen, 1993). The deposits occur both in alluvial plains as 2–3 m thick layers about 2 m below the desert's surface, and infilling fractures in rocks. The dominant arid to hyper-arid climate since at least Miocene time (Clarke, 2006; Rech et al., 2006), and the subsequent lower rates of erosion in this realm

decisively contributed to preservation of the highly soluble salts. A discussion on the formation of these nitrates follows.

Brief Review of Previous Hypotheses

A major obstacle for NO_3 formation is the strong covalent bond (945 kJ mol^{-1} at 298 K) that binds two nitrogen atoms in the form of molecular, atmospheric N_2 (Mather et al., 2004a). However, if an external high energy source can be provided, then the oxidation of N_2 to NO_x can take place (Martin et al., 2006). Previously suggested sources for the Atacama nitrate included bird guano, organic-rich sea spray, microbial nitrogen fixation in the desert soils and playa deposits, ascending hydrothermal fluids, and atmospheric deposition (Ericksen, 1981; Rivera and Stephens, 1988; Chong, 1994; Böhlke et al., 1997; Collao et al., 2002; Michalski et al.,

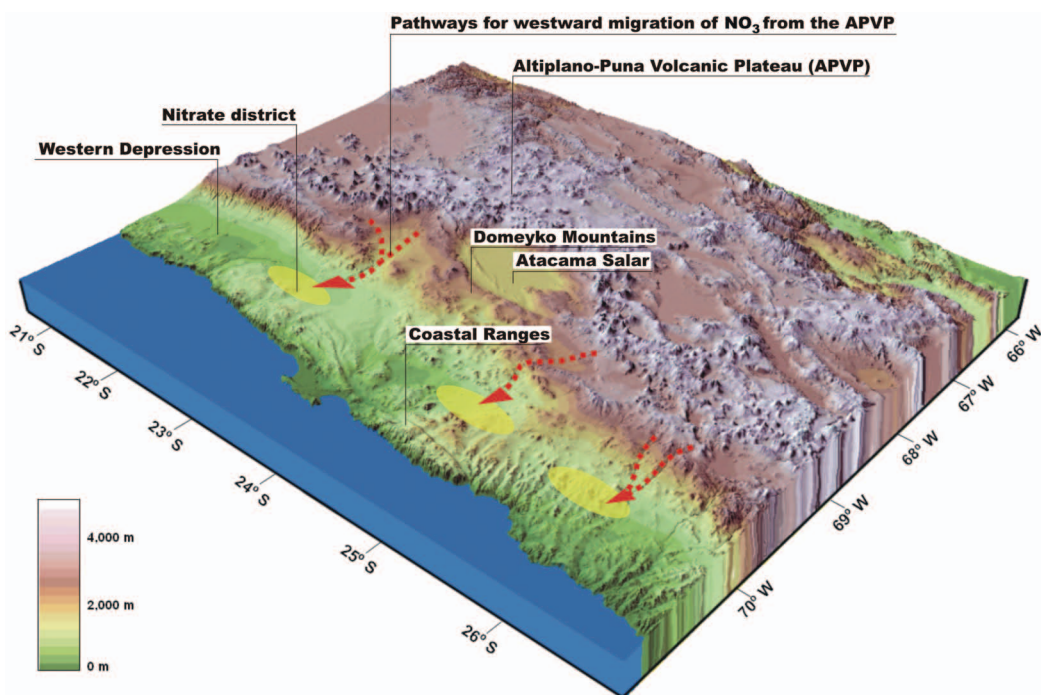


FIG. 2. Digital elevation model (DEM) of the study area (see also Fig. 1) depicting the major structural blocks, simplified location of the main nitrate districts, and corridors (pathways) along which NO_3^- would have been transported westward by surface and groundwater. DEM is based on NASA SRTM data, 90 m resolution (<http://seamless.usgs.gov>).

2004). Ericksen (1983) envisaged a process of nitrogen fixation by bacteria in pre-Andean playa deposits (the so-called Andean *salares*), from where nitrate would have been transported by wind or groundwater to the Western Depression. However, the idea has climatic and geologic problems. On one hand, the prevailing winds blow to the east, that is, in the opposite direction. Besides, the Atacama playa deposits usually occur within endorheic (closed) basins (e.g., the Atacama Salar) (Fig. 2).

Isotopic work on stable isotopes ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) suggests either nitrogen fixation by bacteria or an atmospheric origin for the nitrate (Böhlke et al., 1997). The atmospheric hypothesis was further explored by Michalski et al. (2004), who suggested that the process could be mediated by photochemical reactions involving ozone and atmospheric NO_x ($\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$), which would eventually lead to formation of nitric acid. A reaction of the acid with sea salt or aerosols would result in formation of particulate NO_3 and slow accumulation of nitrates onto the desert surface (Michalski et al.,

2004). However, if this were a plausible explanation, why then are the Atacama nitrate deposits so unique? Why are no equivalent deposits found in other regions of the world where similar conditions are met? For example, the Atacama and Namib deserts are strikingly similar in many aspects, including hemisphere, latitude, cold marine currents along the coast, coastal fogs, and a long-lasting arid climatic history (Partridge, 1993; Clarke, 2006), and yet no nitrate deposits are present in the Namib.

In this respect, despite the many resemblances, there is one major feature that makes the Namib strikingly different from the Atacama Desert: the Namib lacks an active volcanic mountain chain. We here argue that an atmospheric nitrogen source is compatible with a model that involves a key missing link in the “nitrate story”: the coeval formation of the giant Miocene–Pleistocene Altiplano-Puna Volcanic Plateau, lying in front of the nitrate fields (Figs. 1 and 2).

Massive Volcanism at the APVP: The Missing Link

A relationship between volcanism and the nitrate deposits was dismissed on the basis that the $\delta^{15}\text{N}$ values of igneous rocks, and ammonia from fumaroles vents, were generally higher than those of the nitrate deposits (Böhlke et al., 1997). Even if this argument is correct, a major flaw lies within the idea: there is no reason for the nitrogen to be of magmatic origin. Although volcanoes do outgas nitrogen, their output is negligible compared to the concentration of nitrogen in the atmosphere (Mather et al., 2004b). In fact, the nitrogen chemistry of a volcanic plume is likely to be initiated by high-T thermal fixation of atmospheric N_2 and O_2 to form high levels of NO (Martin et al., 2006). These authors go further, indicating that NO would be rapidly oxidized to NO_2 and later converted to HNO_3 by low-temperature chemistry.

The discovery of NO_x in volcanic plumes is not new. However, its origin was only attributed to electrical activity (lightnings) within the plume (e.g., Navarro-González et al., 1998). Volcanic lightning is one of the most outstanding consequences of the electrification of volcanic plumes, and the high temperatures in the lightning channel allow the production of chemical species that otherwise, at ambient conditions, would not form (Mather and Harrison, 2006). Conspicuously, lightning not only fixes nitrogen, but also generates ozone (Desch et al., 2002), a gas also implied in the oxidation of NO_x species ($\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$) (Jaffe, 2000). Lightning activity has been widely reported from many volcanoes in association with eruptions of various types and sizes, and is especially common during larger eruptions (McNutt and Davis, 2000). The atmospheric gases in the current-carrying channel itself are heated to spectroscopically constrained temperatures of $\sim 3 \times 10^4$ K (Desch et al., 2002). At these temperatures, molecules of N_2 are broken and recombined to form compounds of the NO_x type (Desch et al., 2002).

On the other hand, a complete new body of evidence began to form when the plumes from volcanoes such as the Lascar and Villarrica (Chile), Masaya (Nicaragua), and Etna (Italy) were closely monitored from a chemical point of view (Mather et al., 2004a). The volcanoes were not considered as an important part of the global nitrogen cycle until it was shown that they released a previously unconsidered flux of HNO_3 vapor to the atmosphere (Mather

et al., 2004a). Although the precise mechanism for the formation of NO_x - NO_3 remains unclear, it is quite definitive that a process of “thermal fixation” of atmospheric nitrogen followed by rapid oxidation of NO is most likely (Mather et al., 2004a). For example, the nitrogen fixation potential of an eruption of andesitic magma at 1200 K, with a magma density of 2600 kg m^{-3} , and an energy available for nitrogen fixation of 10^5 J kg^{-1} is 10^{10} moles of N_2 per km^3 of erupted magma (Mather et al., 2004b), an impressive amount of nitrogen equivalent to 28×10^4 tons.

Whatever the mechanism (thermal, electric), one thing is clear, provided that enough energy is available, the N-N bond will be broken, and therefore, subsequent oxidation to NO_x will follow inexorably. In the presence of O_2 , N_2 is thermodynamically unstable with respect to aqueous NO_3^- (Jaffe, 2000). In other words, if enough energy is introduced to the system, NO_x compounds will be formed. In any case, lightning and volcanic eruptions are not to be regarded as separate, unrelated processes, as they usually occur together (Mather and Harrison, 2006), and the larger an eruption, the more important the associated electrical activity (McNutt and Davis, 2000). However, despite the fact that both are potential mechanisms for nitrogen fixation, we should also examine a third key element to fully understand the phenomenon: the tephra particles. Formation of salts in the high-T zone, lowermost part of the plume, is followed by condensation as microscopic crystals adsorbed onto the ash particles, a process that would take place at intermediate temperatures (~ 570 – 970 K) (Witham et al., 2005). However, chemical reactions in porous media such as pyroclastic fragments may be more complex, and are important from the viewpoint of chemical reactions. For example, a ceramic porous matrix has a large heat capacity that allows recirculation of heat (Dhamrat and Ellzey, 2006). Furthermore, peak temperatures may exceed the adiabatic equilibrium temperature, and this temperature amplification is due to the large interstitial surface area of the porous media (Dhamrat and Ellzey, 2006). Thus, we may envisage the porous pyroclastic fragments (tephra) not only as particles with large adsorption capacities, but also as efficient natural “chemical reactors” that could further enhance the chemistry of nitrogen fixation. Volcanic plumes from active volcanoes are important sites for nitrogen fixation, and indeed, tephra deposits from different volcanoes have shown the presence of NO_3 (Witham et al.,

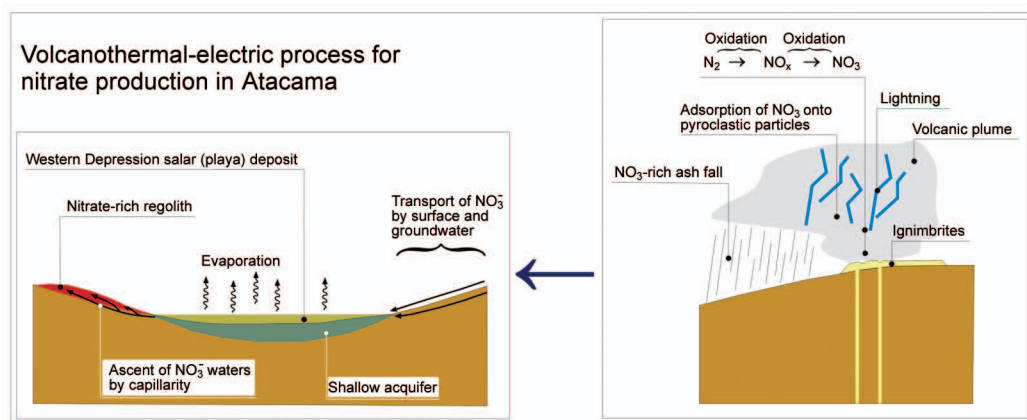


FIG. 3. Simplified model not to scale for thermal and electric fixation of N_2 in the form of NO_3 during massive volcanic activity in the Altiplano-Puna volcanic plateau (right box), and formation of the nitrate deposits within the Western Depression by capillary ascent of NO_3 -rich groundwater through rock fractures and the porous regolith (left box).

2005). Among them we would like to highlight the ashes from the 1993 eruption of the Lascar volcano (APVP), from which $500\text{--}1000\text{ g t}^{-1}$ of NO_3 were obtained during leaching experiments (Risacher and Alonso, 2001).

Taking all this into account, a reasonable mechanism for the generation of the Atacama nitrates would involve the thermal and electric fixation of N_2 in the form of NO_3 during massive volcanism at the APVP, adsorption onto ash particles, leaching of this nitrate from the ash fall deposits, and subsequent transport by surface and groundwater to the Western Depression (Fig. 3). A close examination of the area reveals a number of corridors along which the highly soluble salts could have been westward transported during wetter episodes of this realm in the last 10 Ma (Rech et al., 2006) (Fig. 2). Once in the Western Depression, nitrates would have separated from other less soluble salts, and selectively accumulated by capillary concentration, seeping upward along fractures and through the porous regolith on the lower slopes of the Coastal Ranges (Mueller, 1960) (Fig. 3). This capillary segregation process, operating from groundwater levels in the western, driest band of the central depression, explains the effectiveness of the nitrate concentration process, in contrast with the “salar” (playa) environment, where nitrate did not reach economic grades. The Atacama Desert might be the world’s driest realm, but even today, the longest river of Chile (the Loa River) runs from the Andes to the coast, and groundwater is

extensively present below the dry Atacama surface. Besides, there is a strong westward climatic gradient from the Altiplano to the coast, with summer rains that may reach 30–50 mm in the highest domains, about 6 mm at Calama, and less than 2 mm at Antofagasta (Fig. 1). Thus, independently from climatic variations during the last 10 Ma (wetter and dryer cycles) (Clarke, 2006; Rech et al., 2006), this would explain why preservation of nitrates was only possible at a massive scale along the Western Depression, the driest sector of the Atacama Desert.

Potential for Nitrogen Fixation at the APVP

Although nitrogen fixation in ash during volcanic eruptions appears to be a sound mechanism, it remains to be seen whether this process could account for the formation of the 250 Mt of nitrate present in the Western Depression. Let us make the simple following calculations. 1 km^3 of erupted magma can potentially fix 10^{10} moles of N_2 (Mather et al., 2004b)—that is, $28 \times 10^4\text{ t}$ of N. Given that the total volume of erupted pyroclastic rocks in the APVP in the study area was in the order of 10^4 km^3 , then $28 \times 10^8\text{ t}$ (2,800 Mt) of N could have been fixed. On the other hand, only 16.5% of $NaNO_3$ by weight corresponds to nitrogen, that is, the Atacama deposits contain $\sim 42\text{ Mt}$ N. Thus, the APVP could have fixed 67 times more nitrogen than the required figure to account for the Atacama nitrate deposits. In other words, it does not matter how “inefficient”

the process of fixation and transport might have been, because a mere 1.5% of the total APVP potentially fixed N would easily explain the nitrogen contained in the Atacama nitrate deposits. Concentration of chemical components from a homogeneous source results in a loss of entropy, which is possible because differentiation occurs in conjunction with a greater production of entropy associated with the decay of thermal gradients (Rosing et al., 2006). On the other hand, strong dispersion after initial speciation-concentration of a highly soluble salt is the least we would expect within a scenario such the one here described. Besides, it is reasonable to assume that an important part of the NO_3 must have been directly introduced to the atmosphere.

Volcanoes and the Environment: Concluding Remarks

Volcanic eruptions have far more environmental implications than is usually assumed. Volcanoes not only contributed to the Earth's early atmosphere and hydrosphere, and from there, to set the bases for the origin of life, but continue today to contribute to the global cycles of many chemical elements and compounds. Volcanic activity, either violent, with massive introduction of volcanic aerosols to the atmosphere, or via quiescent degassing, steadily modify the environment (e.g., Rampino and Self, 1992; Matsumoto and Hinkley, 2001; Mather et al., 2004a, 2004b; Oppenheimer, 2004; Oyarzun et al., 2005; among others). This can occur at a massive scale as shown by the eruption of Pinatubo (Philippines) in 1991, when the volcanic column injected the tropopause at an altitude of ~ 17 km, introducing $\sim 20 \times 10^{12}$ g of SO_2 to the stratosphere (Oppenheimer, 2004), or even larger if we consider the Toba eruption in Indonesia (~ 74 Ka), which introduced an estimated $\sim 3 \times 10^{15}$ g of $\text{H}_2\text{S} + \text{SO}_2$ into the atmosphere (Rampino and Self, 1992).

An example relevant to the cycle of NO_x compounds was provided by Gallardo and Rodhe (1997), who indicated that simulations of oxidized nitrogen performed with global transport tracer models systematically underestimate the concentrations of total nitrate in the pristine atmosphere at remote marine locations in the mid-Pacific. These authors suggested that the extra source of NO_x emission could be provided by additional (cloud-to-cloud) lightning activity, or by "an unknown source" of NO_x over the Pacific Ocean. In this respect, we should bear in mind that the mid-Pacific is central

to the Earth's largest concentration of volcanoes—that is, the so-called Ring of Fire—and therefore, besides lightning activity, volcanism could easily account for this excess of NO_x .

Finally, it is a well-known fact that volcanic soils in tropical-subtropical regions are extremely fertile compared to those of non-volcanic regions. Perhaps the reason goes beyond the mere absorption of chemical elements by plants (which is increased by the easy weathering and breakdown of igneous minerals in such regions), and may reflect enhanced availability of nitrogen, a key nutrient. It might turn out that volcanic activity naturally fertilizes the ground by adding nitrate to the system, which would compensate for the initial adverse effects of ash falls. Whatever the case, we should keep in mind that the importance of volcanic activity should never be underestimated.

Acknowledgments

We thank Javier Lillo and Francisco Carreño (URJC) for the digital elevation model of northern Chile. This work was partly supported by Grant CTM2006-13091-C02-01 (Ministry of Science and Education, Spain).

REFERENCES

- Allmendinger, R. W., Jordan, T. E., Kay, S. M., Isacks, B. L., 1997, The evolution of the Altiplano-Puna plateau of the central Andes: Annual Review of Earth and Planetary Sciences, v. 25, 139–174.
- Babeyko, A. Y., Sobolev, S. V., Trumbull, R. B., Oncken, O., and Lavier, L. L., 2002, Numerical models of crustal scale convection and partial melting beneath the Altiplano-Puna plateau: Earth and Planetary Science Letters, v. 199, p. 373–388.
- Böhlke, J. K., Ericksen, G. E., and Revesz, K., 1997, Stable isotope evidence for an atmospheric origin of desert nitrate deposits in northern Chile and southern California: Chemical Geology, v. 136, p. 135–152.
- Chong, G., 1994, The nitrate deposits of Chile, in Reutter, K. J., Scheuber, E., and Wigger, P. J., eds, Tectonics of the southern central Andes: Structure and evolution of an active continental margin: Berlin, Germany, Springer-Verlag, p. 303–316.
- Clarke, J. D. A., 2006, Antiquity of aridity in the Chilean Atacama Desert: Geomorphology, v. 73, p. 101–114.
- Collao, S., Arce, E., and Andía, A., 2002, Mineralogía, química, e inclusiones fluidas en los depósitos de nitratos de María Elena, II Región Chile: Boletín de la Sociedad Chilena de Química, v. 47, p. 181–190.

- De Silva, S. L., 1989, Altiplano-Puna volcanic complex of the central Andes: *Geology*, v. 17, p. 1102–1106.
- Desch, S. J., Borucki, W. J., Russell, C. T., and Bar-Nun, A., 2002, Progress in planetary lightning: Reports on Progress in Physics, v. 65, p. 955–997.
- Dhamrat, R. S., and Ellzey, J. L., 2006, Numerical and experimental study of the conversion of methane to hydrogen in a porous media reactor: *Combustion Flame*, v. 44, p. 698–709.
- Ericksen, G. E., 1981, *Geology and origin of the Chilean nitrate deposits*: United States Geological Survey, Professional Paper 1188, 37 p.
- Ericksen, G. E., 1983, The Chilean nitrate deposits: *American Scientist*, v. 71, p. 366–374.
- Ericksen, G. E., 1993, Upper Tertiary and Quaternary continental saline deposits in the central Andean region, in Kirkham, R. V., Sinclair, W. D., Thorpe, R. I., and Duke, J. M., eds, *Mineral deposits modelling*: Geological Association of Canada, Special Paper 40, p. 89–102.
- Gallardo, L., and Rodhe, H., 1997, Oxidized nitrogen in the remote Pacific: The role of electrical discharges over the oceans: *Journal of Atmospheric Chemistry*, v. 26, p. 147–168.
- Jaffe, D. A., 2000, The nitrogen cycle, in Jacobson, M. C., Charlson, R. J., Rodhe, H., and Orians, G. H., eds., *Earth system science*: San Diego, CA, Academic Press, p. 322–342.
- Martin, R. S., Mather, T. A., and Pyle, D. M., 2006, High-temperature mixtures of magmatic and atmospheric gases: *Geochemistry, Geophysics, Geosystems*, v. 7, p. 1–14.
- Mather, T. A., Allen, A. G., Davison, B. M., Pyle, D. M., Oppenheimer, C., and McGonigle, A. J. S., 2004a, Nitric acid from volcanoes: *Earth and Planetary Science Letters*, v. 218, p. 17–30.
- Mather, T. A., and Harrison, R. G., 2006, Electrification of volcanic plumes: *Surveys in Geophysics*, v. 27, p. 387–432.
- Mather, T. A., Pyle, D. M., and Allen, A. G., 2004b, Volcanic source for fixed nitrogen in the early Earth's atmosphere: *Geology*, v. 32, p. 905–908.
- Matsumoto, A., and Hinkley, T. K., 2001, Trace metal suites in Antarctic pre-industrial ice are consistent with emissions from quiescent degassing of volcanoes worldwide: *Earth and Planetary Science Letters*, v. 186, p. 33–43.
- McNutt, S. R., and Davis, C. M., 2000, Lightning associated with the 1992 eruptions of Crater Peak, Mount Spurr Volcano, Alaska: *Journal of Volcanology and Geothermal Research*, v. 102, p. 45–65.
- Michalski, G., Böhlke, J. K., and Thieme, M., 2004, Long-term deposition as the source of nitrate and other salts in the Atacama Desert, Chile: New evidence from mass-independent oxygen isotopic compositions: *Geochimica et Cosmochimica Acta*, v. 68, p. 4023–4038.
- Mueller, G., 1960, The theory of formation of north Chilean nitrate deposits through capillary concentration, in 21st International Geological Congress. Part 1, geochemical cycles: Copenhagen, Denmark, Det Berlingske Bogtrykkeri Press, p. 76–86.
- Navarro-González, R., Molina, M. J., and Molina, L. T., 1998, Nitrogen fixation by volcanic lightning in the early Earth: *Geophysical Research Letters*, v. 25, p. 3123–3126.
- Oppenheimer, C., 2004, Volcanic degassing, in Rudnick, R. L., ed., *Treatise on geochemistry*, Volume 3 (The crust): Amsterdam, The Netherlands, Elsevier, p. 123–166.
- Oyarzun, R., Lillo, J., Sánchez Hernández, J. C., and Higuera, P., 2005, Pre-industrial metal anomalies in ice cores: A simplified reassessment of windborne soil dust contribution and volcanic activity during the last glaciation: *International Geology Review*, v. 47, p. 1120–1130.
- Partridge, T. C., 1993, The evidence for Cainozoic aridification in southern Africa: *Quaternary International*, v. 17, p. 105–110.
- Rampino, M. R., and Self, S., 1992, Volcanic winter and accelerated glaciation following the Toba super-eruption: *Nature*, v. 359, p. 50–52.
- Rech, J. A., Currie, B. S., Michalski, G., and Cowan, A. M., 2006, Neogene climate change and uplift in the Atacama Desert, Chile: *Geology*, v. 34, p. 761–764.
- Risacher, F., and Alonso, H., 2001, Geochemistry of ash leachates from the 1993 Lascar eruption, northern Chile. Implications for recycling of ancient evaporates: *Journal of Volcanology and Geothermal Research*, v. 109, p. 319–337.
- Rivera, S., and Stephens, A. J., 1988, Campos geotermiales fósiles de edad Terciario Inferior y mineralización asociada, en la Región de Antofagasta, in 5th Chilean Geologic Congress, Santiago, v. 1, p. B39–B64.
- Rosing, T., Bird, D. K., Sleep, N. H., Glassley, W., and Albarede, F., 2006, The rise of the continents—an essay on the geological consequences of photosynthesis: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 232, p. 99–113.
- Schmitt, A. K., Kasemann, S., Meixner, A., and Rhede, D., 2002, Boron in central Andean ignimbrites: Implications for crustal boron cycles in an active continental margin: *Chemical Geology*, v. 183, p. 333–347.
- Witham, C. S., Oppenheimer, C., and Horwell, C. J., 2005, Volcanic ash-leachates: A review and recommendations for sampling methods: *Journal of Volcanology and Geothermal Research*, v. 141, p. 299–326.